Final Report, SERDP Project 1241

I. Project title: A Novel Laser Ionization and Modeling Approach for the Determination of Soot Nucleation Mechanisms

II. Performing organizations (investigators): US Army Research Laboratory (Dr. William R. Anderson and Dr. Rosario C. Sausa) and New Jersey Institute of Technology (Prof. Joseph W. Bozzelli)

III. Project background: The SERDP statement of need that led to this research project focuses on a requirement for better models of the mechanisms of soot formation in combustion. Soot and its combustion precursors present human health hazards. In the case of Army fighting vehicles, such as those powered by diesel engines, it is of interest to achieve the maximum possible power density. One way to do this is to run at high fuel/oxidizer ratios. However, this gives rise to high soot pollutant emissions. While they are important, health issues of the soot are not the only issue and are not the utmost concern during battle. High soot emission levels in combat vehicles may give rise to large target signatures, thus adversely affecting survivability. In the report of the SERDP-sponsored June 1999 American Academy of Environmental Engineers Air Quality Workshop [1], a major conclusion is that "chemical kinetics and aerosol dynamics governing formation and control of PM (particulate material such as soot) and associated HAPs (Hazardous Air Pollutants, such as PAH, Polycyclic Aromatic Hydrocarbons, which are precursors of soot) is a primary area needing research." The report goes on to state that models which use presently available mechanisms are in need of refinements to achieve agreement with experiments and predictive capabilities. A fundamental understanding of the factors and detailed chemistry that govern the formation and destruction of soot and its precursors is important for the identification of control methods. This project centered upon the chemical kinetics mechanism.

For several decades there has been a controversy in soot formation whether ion or free radical mechanisms dominate the early, nucleation stages of the process starting with molecules containing only one or a few carbon atoms; of course, one or the other may dominate under a variety of conditions. Nucleation mechanisms involving ions have fallen into disfavor in the eyes of many researchers. One notes that discussions amongst the researchers involved seem to have become somewhat polarized. Also, there may be an influence from a natural tendency to favor study of radical mechanisms because more is known about them and the high temperature kinetics experimental methods to study neutral species are well established; that is not the case for ions. However, the issue of whether ions play a role has never been satisfactorily resolved. The difficulty arises partly from the fact that experiments to probe the small precursor ions are very difficult because concentrations of the ions are quite small. (In proposed ion soot mechanisms it is argued that very large rate constants compensate for these low concentrations so that rates of the ion-molecule nucleation reactions are nevertheless large.) In addition, the high temperature chemistry of ions has not received nearly as much attention as radical chemistry. Thus, the rate constant and thermodynamic databases are not extensive at high temperatures for species and reactions of interest in the ion mechanism.

IV. Objectives: To ascertain the role of ion-molecule reactions during soot nucleation in simple flames using laser spectroscopic experiments and modeling calculations.

Report Documentation Page

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **OCT 2001**	2. REPORT TYPE	3. DATES COVERED **00-00-2001 to 00-00-2001**
4. TITLE AND SUBTITLE **A Novel Laser Ionization and Modeling Approach for the Determination of Soot Nucleation Mechanisms**		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **US Army Research Laboratory,2800 Powder Mill Road,Adelphi,MD,20783-1197**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**		
13. SUPPLEMENTARY NOTES		
14. ABSTRACT		
15. SUBJECT TERMS		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT **Same as Report (SAR)**	18. NUMBER OF PAGES **13**	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**			

V. Technical Approach: Develop detailed chemical mechanism for C_2H_2/O_2 flame and model the formation of HCO^+ and other ions pertinent to the formation of larger hydrocarbons, e.g. PAH and PAH^+. Validate model using laser-induced resonance ionization (REMPI) to create ions in C_2H_2/O_2 flames and then monitor the formation of soot or soot precursors by molecular beam mass spectrometry (MBMS) or laser-induced incandescence (LII). In particular, create HCO^+ ions in flames using REMPI on HCO. Then measure change in PAH and PAH^+ formed as a result by MBMS or LII. Alternatively, create HCO^+ ions by exciting CH in flames, by means of the $CH^* + O$ reaction, and/or measure change in soot formation directly via LII. In addition, perform experimental and modeling studies of CH_4/CH_3OH mixtures under pyrolytic and oxidative conditions; the mechanism extends small fuel molecule chemistry to high fuel/oxidizer ratios and high pressures as a basis for future modeling of soot formation.

VI. Summary:

Began modifications to MBMS detection system appropriate for the detection of ions. These could not be completed due to delays in our procurement system.

Identified LII as an alternate, complimentary approach for detection of soot. Established ability to detect LII in our flames using a Nd:YAG pump laser.

Identified CH excitation followed by reaction with O atoms as a possible alternate approach to form HCO^+ ions in flames.

Fabricated flame ion detection electrodes and established that they can detect REMPI of NO in cold flows and flames.

Initial ionic soot formation mechanism developed and modeling of combustion community 'standard' C_2H_2 flame completed. Mechanism includes improved (this work) thermodynamics for over 100 species and reactions for a new species, C_3H_2, which is important in the initial conversion of $C_3H_3^+$ to larger HC ions.

Determined kinetic and thermochemical kinetic parameters for vinylidene formation and vinylidene insertion reactions to chain branching for soot. These are promising new reaction paths for soot formation.

Developed a detailed, pressure dependent reaction model for methane/methanol mixtures under pyrolytic and oxidative conditions and compared the results with experiment.

Published one paper in the open literature and made three presentations (see Section VIIA). A second manuscript describing calculation of thermochemistry parameters (mentioned in fifth item above) for over 100 soot-related species is in preparation.

VII. Project accomplishments

A. Papers/presentations:

(1) Wen-chium Ing, Chad Y. Sheng, and Joseph Bozzelli, "Detailed, Pressure Dependant Reaction Model for Methane/Methanol Mixtures Under Pyrolytic and

Oxidative Conditions and Comparison with Experiment", Fuel Processing Technology, in press.

(2) C. Sheng and J.W. Bozzelli, "Thermochemistry, Reaction Paths and Kinetic Parameters in Hydrocarbon Pyrolysis and Oxidation," Symposium on Applications of Computational Chemistry in Petroleum Chemicals, ACS Meeting, Orlando, FL, April 2002.

(3) C. Sheng and J.W. Bozzelli, "Thermochemical Parameters, Enthalpies, Entropies and Heat Capacities of Hydrocarbons and Oxygenated Hydrocarbons Reactions Important in Chain Branching," 2002 International IUPAC Chemical conference on Thermodynamics, Rostock, Germany, July 22 – 26, 2002.

(4) W.R. Anderson, R.C. Sausa, and J.W. Bozzelli, "Novel Laser Ionization and Modeling Techniques for the Determination of Soot Nucleation Mechanisms," U.S. Army Industrial Ecology Information Exchange Meeting, Lake Harmony (Split Rock), PA, June 25-27, 2002.

B. Results/Discussion

    (1) Experimental efforts

    A schematic of the existing experimental apparatus is shown in Fig. 1. This apparatus has been used in many experiments; further details may be found in representative publications on NO_x related flames [2]. Briefly, fuel/O_2 flames (fuel = CH_4, C_2H_4 or C_2H_2) are stabilized on a cylindrical, flat burner (McKenna Products) contained in a stainless steel vacuum chamber. The burner section is maintained at pressures from a few torr to one atm; typically, tens of torr are used. The reactant gases are flowed through inlets at the bottom of the apparatus into the burner where mixing occurs. They flow out through a sintered (thus porous), stainless steel plug mounted at the top surface of the burner, yielding a flat, one-dimensional flow. The plug is encircled by another sintered porous plug through which argon is typically flowed, thus forming a protective sheath of inert gas around the flame and minimizing the effects of recirculating burnt gases. The burner is mounted on a feedthrough/linear motion translator that allows precision horizontal and vertical scanning of the burner with respect to detectors. This allows sampling at different positions within a flame. Temperature profiles are measured by using fine-wire Pt/Pt-Rh thermocouples, shown just above the burner (see Fig. 1). Alternatively, the thermocouple may be moved off center so that laser beams may be guided through the optical ports (lasers and beams not shown). A number of laser techniques, such as LIF (laser induced fluorescence) and REMPI, may be used for measurement of temperature and/or species concentration profiles in the flame. Finally, the upper half of the diagram displays the MBMS detector. The mass spectrometer is an Extrel C50 TQMS inline triple quadrupole mass filter with a concentric axis electron ionizer. By utilizing the second and third stages of the mass filter, ions of equal m/e ratio, but differing formula (e.g. CO_2 and N_2O) or isomeric structure, may be separated. This feature applies whether the mass spectrometer's ionizer source or REMPI is used to make the ions. For the unmodified system, neutral flame gases are sampled through a conical quartz-sampling cone with a 200-micron diameter orifice. Sampled flame gases expand supersonically in the space behind the sampling cone, the pressure in this
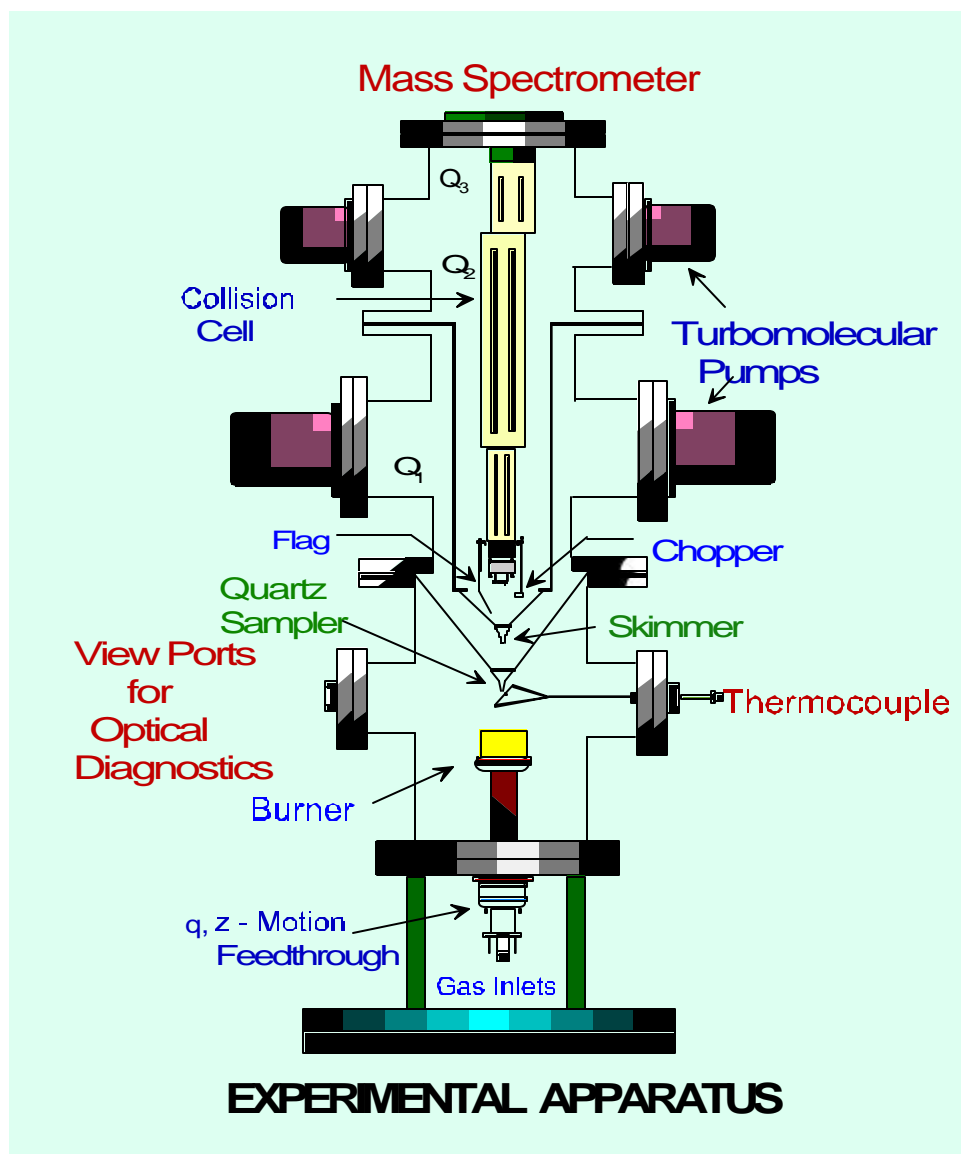
Fig. 1. Schematic of Experimental Apparatus

section being maintained at 5×10^{-5} torr. The expanding gases are collimated through a second, nickel-plated skimmer with orifice diameter 2 mm. The sampled gases then pass into the ionization region of the first quadrupole, which is maintained at 2×10^{-6} torr. The modifications we had planned to the system, which did not materialize because of procurement delays, would have allowed electrical biasing of the sampling and skimmer cones, especially the latter, at a few volts to allow for sampling, and mass identification, of ions. This technique greatly increases sensitivity [3] to ions. The method has a detection sensitivity for nascent flame ions of about 10^6 to 10^7 ions/cm^3 [3,4]. Absolute concentrations of the ions can be determined by a technique described in Ref. [4]. The technique is clearly applicable, and has been used, for nascent flame ions where concentrations are of the order 10^9 ions/cm^3 [4,5]. Unfortunately, additional funding to continue the project into a second year was not available. Were it made available, we

would complete modifications to the system and, in this way, continue efforts to detect the spectrum of ions formed due to chemistry following the injection of HCO[+] into the flame by one of the two laser spectroscopic techniques discussed below. We believe this would have more sensitivity to soot chemistry than the other approach we tried and allow us to better address the fundamental issue of whether ion chemistry is important in soot nucleation.

We identified LII [6] for the detection of soot. This method has an advantage over the MBMS probe for ions that it directly detects soot, so if soot signal could be detected upon laser injection of HCO[+], this approach could yield very convincing evidence for the ion nucleation mechanism. Its disadvantages are that it is less sensitive and no direct information on the ionic reaction pathways to soot formation (that is, what species are involved) can be obtained in this way. In LII, a laser beam is focused in a sooting flame. The soot absorbs some of the monochromatic laser light and is heated. The hot soot then emits blackbody radiation with a wavelength and temporal dependence that is dependent on the size of the soot particles [6]. An example, obtained in the present work, is shown in Fig. 2. A pulsed, Nd: YAG pumped dye laser was used as the excitation source. The LII was excited in a slightly rich, C_2H_4/O_2 flame burning at 30 torr in our low-pressure system (described more fully in the next paragraph). LII emission was excited using the fundamental 1.06 μm output of a Nd:YAG laser with a modest energy of 275 mJ/cm^2. Detection was at right angles to the laser beam using a photomultiplier with filter centered at 700 nm. The negative-going pulse at 0.28 μsec in Fig. 2 is spurious electronic pickup due to the laser pulsing electronics. The laser pulse occurred at about 0.34 μsec and had duration of about 10 nsec. The LII decay after the

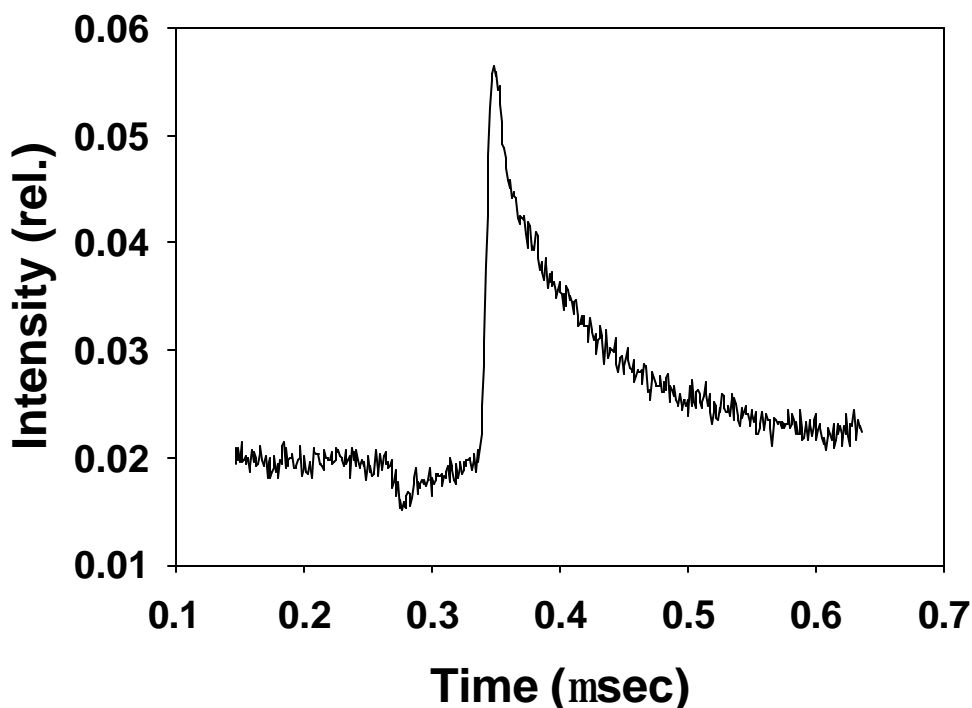Fig. 2. Example LII signal obtained in a rich C_2H_4/O_2 flame at 37 torr.

5

laser pulse obviously has a much longer duration. Proof that the signal arises from soot was obtained by adjusting the flame to a leaner, non-sooting condition, which results in disappearance of the signal.

Our original idea to perturb the flame HCO^+ concentration, presented in the proposal, was to use REMPI excitation of the nascent HCO neutral species. During the course of the research we identified a possible alternative approach from the literature: single photon excitation of CH in the flame to an electronic excited state (which does not require high laser power so that the laser operation does not always have to be optimized), followed by reaction of the excited CH with atomic oxygen, vis: $CH^* + O = HCO^+ + e$, where CH^* represents electronically excited, neutral CH. This approach to formation of HCO^+ in flames has been demonstrated by Cool and Tjossem [7] and used for the measurement of high temperature rate constants of the ionization reaction. It is viable because the rate of reaction of CH* with O is much larger than for ground state CH with O. The approach would have significant advantages over REMPI on HCO, if viable, in particular that an unfocused laser beam may be used because the absorption is a single photon process. Because the multiphoton nature of the absorption necessitates a very high laser power, REMPI requires a focused laser beam. The necessity of focusing complicates both the experiment and the modeling that would ultimately result. In both approaches, the simplest way to detect whether ions are being formed is by use of an ion probe, which is simply a heat-shielded, electrically biased wire probe placed within the flame, close to the focal point of the laser beam. We were readily able to detect REMPI signals from NO by this method, both in cold, unreactive flows and in flames. This was used primarily as a simple technique to standardize and calibrate the system. NO signals from both types of sources are shown in Figs. 3 and 4.
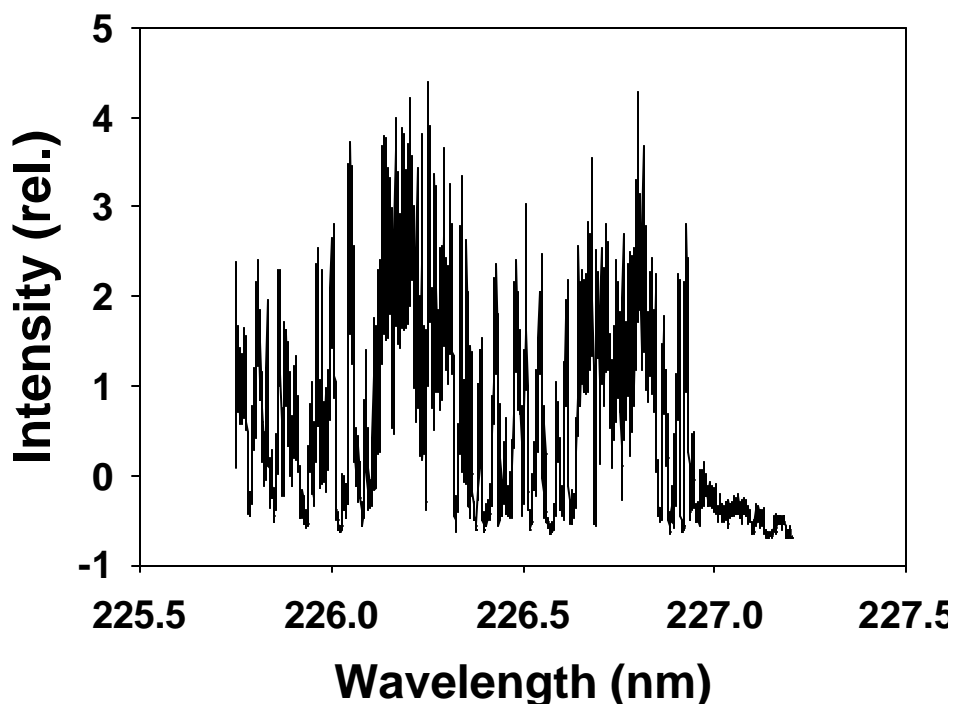

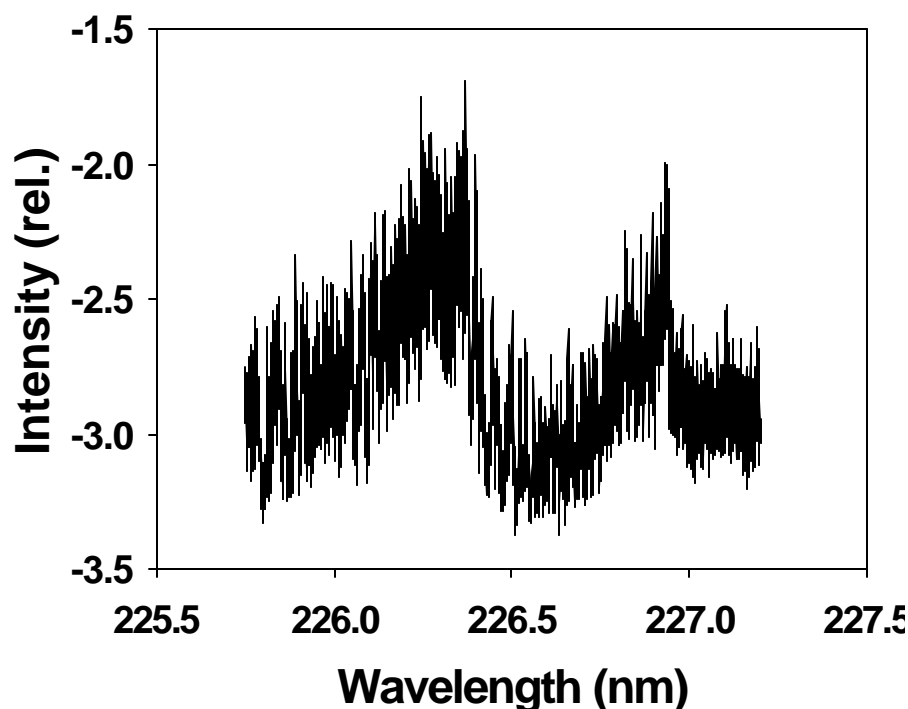Fig. 3. REMPI spectrum of NO in a cold flow of 0.1% NO in Ar at 1 atm.

6

Fig. 4. NO REMPI spectrum in a low-pressure $CH_4/O_2/Ar$ flame
seeded with about 100 ppm NO.

The wavelength dependence clearly identifies the signal as arising from NO. However, at present we have, surprisingly, been unsuccessful in attempts to be certain whether we were creating a significant quantity of HCO^+ ions in a flame by either of the methods described above. We believe that it should be possible to do this, especially by the REMPI technique since one of us (Sausa) was heavily involved in some of the earliest experiments in which that diagnostic was developed and applied to HCO in a variety of flames [8]; and also since our modeling calculations indicate sufficient HCO should be present, both in lean, non-sooting flames, and rich, sooting flames. Probably our difficulties in this regard center on the small concentration of HCO in flames, and the multitude of variables (laser intensity, focusing, position in the flame, wavelength) that need to be simultaneously adjusted to achieve significant HCO^+ formation. Due to the unexpected REMPI difficulties, a sample of acetaldehyde (CH_3CHO) was ordered to facilitate the adjustment of the system variables; it is well-known that large quantities of HCO can be made by photolysis of CH_3CHO, making optimization of system parameters simpler so that the signal can be found, laser conditions optimized, and then REMPI can then be applied in flames. The sample was not received prior to the end of the project. Were additional funding made available, we would further pursue both approaches to making HCO^+ in flames, and we would expect ultimate success in answering the key question.

As stated previously, we attempted to use single-photon excitation of CH, followed by enhanced reaction of CH^* with O atoms [7] as an alternate approach to

create HCO$^+$ ions in flames. One may insure that CH is excited by monitoring its laser induced fluorescence (LIF) signal. An example LIF spectrum obtained in this work in a slightly lean C$_2$H$_4$/O$_2$/Ar flame at 16 torr is shown in Fig. 5. The detector was a photomultiplier with filter centered at 400 nm. Observation of the LIF insures that CH is pumped into the excited state. While the laser was 'parked' on one of the excitation lines shown in Fig. 5, we had the same ion probe as used for REMPI detection in the flame. Unfortunately we were not able to detect a signal and thus conclusively prove HCO$^+$ was being made in this way. Perhaps conditions and/or position of the excitation beam within the flames did not exactly replicate those of Ref. [7].
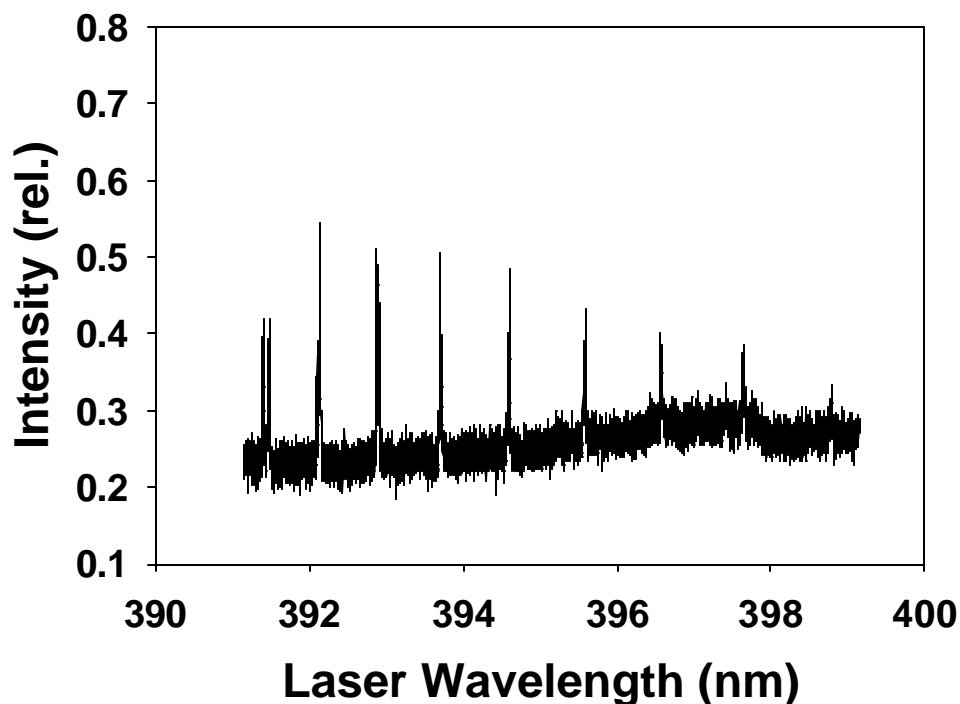

Fig. 5. LIF spectrum of CH in a C$_2$H$_4$/O$_2$/Ar flame at 16 torr.

In spite of our lack of assurances that HCO$^+$ was being made in our flames, we did attempt to detect soot (or increases in soot density) in flames of mixture ratios just below and above the soot point using a two-laser, pump-probe method with LII as the probe technique. This was done with flames of CH$_4$/O$_2$ and C$_2$H$_4$/O$_2$ at both atmospheric pressure and low pressure, and, for the dye laser, (1) using REMPI ionized NO, (2) attempting to scan the laser through the REMPI region for HCO, and (3) with the laser parked on a CH excitation. For the first method we were hoping NO$^+$ would undergo charge transfer reactions with HCO or hydrocarbons and lead to soot formation. For the latter two, we were hoping that the laser excitation was causing some HCO$^+$ formation in spite of our lack of signal at the REMPI probe. (Basically here, we were suspecting there might be something wrong with the REMPI probe causing a reduced sensitivity.)

We have thus far been unable to successfully detect a change in sooting level in these experiments. We would continue were further funding available. Although we were successful in putting NO^+ ions in the flames, there is no guarantee these would charge exchange with other flame molecules in the way we hope, providing a good test. The main purpose of using it is for setup of the system, since it is easy to inject and detect its REMPI signal. And we were unable to be properly certain we were creating HCO^+ in the other experiments. Were further funding made available, we would continue the efforts to make HCO^+, primarily via REMPI and beginning with photolysis of CH_3CHO, where we feel virtually assured of success because we can make a large amount of HCO in this way and, once the laser is on the correct wavelength, adjust whatever variable(s) is causing our detection problem. We *know* that this can be done in these flames because we have done it in the past. Then, once we are certain HCO^+ is being formed in the flames, we can follow a logical progression using both LII and the MBMS to probe whether soot is formed. Once we have the answer to this key question, we would continue using the MBMS to probe either the ion or neutral soot nucleation chemistry, as appropriate, and study it.

B. Modeling Efforts

A significant amount of progress was made on modeling connected with soot formation: (1) initial modeling of hydrocarbon ion growth in flames, (2) improvement of the thermodynamics for over 100 species involved in the ion soot formation mechanism, and (3) modeling of soot formation in methane/methanol mixtures under pyrolytic and oxidizing conditions was performed. These items are discussed, in order, in the following 3 paragraphs.

We obtained from H. Calcote, the world's leading proponent of the ion soot theory, his most recent mechanism for hydrocarbon ion formation in flames. We modeled a $C_2H_2/O_2/Ar$ flame under conditions that have been used as a 'standard' for many soot studies. Runs with his mechanism resulted in predicted HC^+ (here HC^+ will be a general symbol representing large hydrocarbon ions) much too low. We determined that the most probable reason for this is that the neutral C_3H_2 species, and reactions involving it, had been left out of the mechanism. In particular, the reaction:

$$HCO^+ + C_3H_2 = CO + C_3H_3^+ \qquad\qquad\qquad (R1)$$

is the most likely explanation for conversion of the ion initially formed, HCO^+, to an HC^+ ion which can then undergo growth. We currently have new reactions in the mechanism that lead to the formation of C_3H_2, but the concentrations of C_3H_2 and subsequently-formed HC^+ are currently being severely over-predicted. Probably this results because R1 is the only reaction currently being included for consumption of C_3H_2. Other species present in high concentration, such as O2, can react very rapidly with C3H2 reducing the concentration and should be included. Were continuation funding available, we would expand the mechanism include these important reactions and increase fidelity of the model. Predicted concentration profiles of several species are given in Figs. 6 and 7.

The thermodynamics of most of the ionic species in Calcote's mechanism was estimated by group additivity methods. Improved calculations for the thermochemistry of over 100 soot related species has been improved via density functional calculations. Thermochemical parameters for heat of formation, entropy, and heat capacity, and their

temperature dependence have been determined. Fits to the functional form commonly used in CHEMKIN calculations have been provided. A manuscript describing these results is in preparation.

Finally, modeling of methane/methanol mixtures pyrolysis and combustion was performed. The work extends small fuel molecule chemistry models to high fuel/oxidizer ratios, forming the basis for future soot modeling. A paper describing the work is given in the appendix.
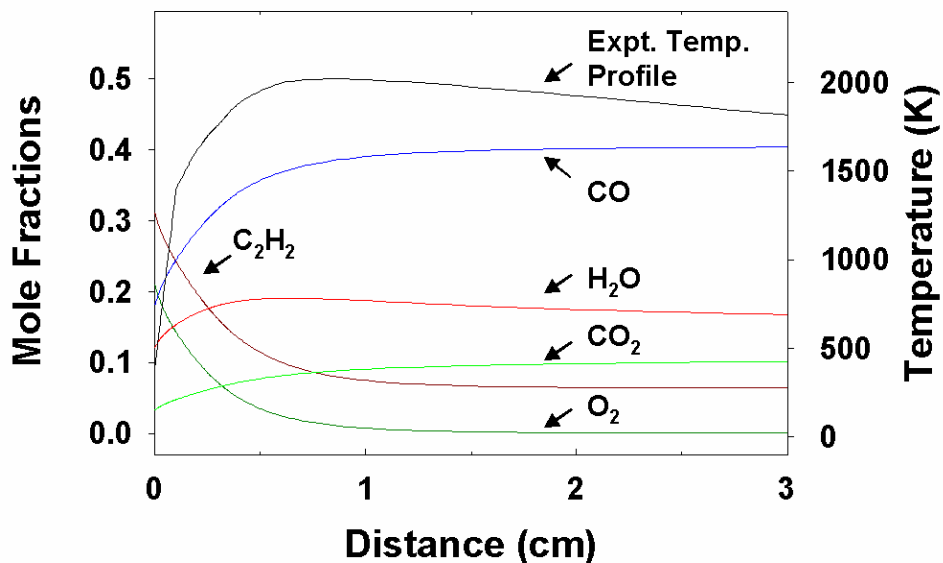

Fig. 6. Predicted majority species profiles for a rich $C_2H_2/O_2/Ar$ flame at 20 torr.
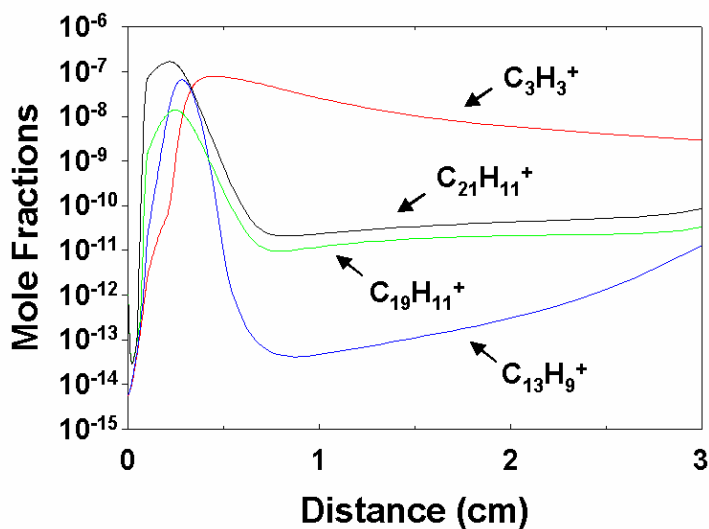

Fig. 7. Predicted concentrations of some HC ions in a rich $C_2H_2/O_2/Ar$ flame at 20 torr.

VIII. Conclusions: We performed theoretical studies in conjunction with the experimental efforts to extend the chemical kinetics and thermodynamics databases relevant to both ion and radical soot nucleation mechanisms. Important additions to the thermodynamics (over 100 soot related chemical species) of ion and neutral chemistry and an important new neutral species pathway pertinent to soot formation were made and will be published. We believe that the role of ion-molecule reaction can be determined given additional funds and time.

IX. Transition Plan: Our results will be published in the open literature. Presently 1 paper and 3 presentations resulting from the work have been published. We expect one further paper will result from the research thus far performed. See section VII and Appendix A.

X. Recommendations: This effort was treated as a SEED project for one year funding. We recommend future funding so that the following work can be accomplished:
(A) If we determine ions are important to soot nucleation, then we will continue to complete experiments and modeling pertinent to the ion mechanism; and (B) If ions are found to not be important in soot nucleation, we will study the effects of radical species seeded into flames on soot formation. For either plan A or B, we will continue performing pertinent computational chemistry for mechanism development. We will model the experimental results to test the mechanism.

We will provide a soot nucleation model with detailed kinetics and thermodynamics to the following laboratories: (1) MURI in Diesel Engine Research at Univ. Wisc. (Chris Rutland); (2) TACOM (Walter Bryzik); (3) VPD/ARL (Robert Bill); (4) AFOSR (Julian Tischkoff); and (4) other DOD and DOE laboratories, and various industries interested in diesel applications. Dr. Anderson has served on the review panel for the Univ. Wisc. MURI for the past 10 years and has interacted with the MURI investigators, TACOM, AFOSR, VPD/ARL, and industrial representatives. We will of course publish results in the open literature.

References

1. W.C. Anderson, "Research Needs Related to Improving Air Emissions from Diesel Engines, Gas Turbines, and Ordnance," report of the American Academy of Environmental Engineers for the December 1998 SERDP sponsored workshop, June 1999.

2. (a.) R.C. Sausa, W.R. Anderson, D.C. Dayton, C.M. Faust, and S.L. Howard, "Detailed Structure Study of a Low Pressure Stoichiometric $H_2/N_2O/Ar$ Flame", *Combust. Flame* 94, p. 407, 1993. (b.) D.C. Dayton, C.M. Faust, W.R. Anderson, and R.C. Sausa, "Flame Structure Study of a Lean $H_2/N_2O/Ar$ Flame Employing Molecular Beam Mass Spectrometry and Modeling", *Combust. Flame* 99, 323, 1994. (c.) R.C. Sausa, G. Singh, G.W. Lemire, and W.R. Anderson, "Molecular Beam Mass Spectrometric and Modeling Studies of Neat and NH_3 Doped Low pressure $H_2/N_2O/Ar$ Flames: Formation and Consumption of NO", *Twenty-Sixth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, PA) Vol. I, p. 1043, 1996.

3. P. Michaud, J.L. Delfau, and A. Barassin, "The Positive Ion Chemistry in the Post-Combustion Zone of Sooting Premixed Acetylene Low Pressure Flat Flames," *Eighteenth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1981), p. 443.

4. Ph. Gerhardt, S. Loffler, and K.H. Homann, "The Formation of Polyhedral Carbon Ions in Fuel-Rich Aetylene and Benzene Flames," *Twenty-Second Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1988), p. 395.

5. H.F. Calcote and R.J. Gill, "Comparison of the Ionic Mechanism of Soot Formation with a Free Radical Mechanism," in *Soot Formation in Combustion, Mechanism and Models*, H. Bockhorn, Ed., Springer Series in Chemical Physics no. 59 (Springer-Verlag, NY, 1994), p. 417.

6. B. Mewes and J.M. Seitzman, "Soot Volume Fraction and Particle Size Measurements with Laser-Induced Incandescence," Appl. Optics 36, 709, 1997.

7. T.A. Cool and P.J.H. Tjossem, "Direct Observations of Chemi-Ionization in Hydrocarbon Flames Enhanced by Laser Excited CH* (A $^2\Delta$) and CH* (B $^2\Sigma^-$)," *Chem. Phys. Lett.* 111, p. 82, 1984.

8. (a.) S.L. Howard, R.C. Sausa, and A.W. Miziolek, "Mass spectrometric study of simple olefinic flames: comparison with laser diagnostics of $C_2H_4/O_2/Ar$ flames at 20 Torr," *Rapid Communications in Mass Spectrometry* 6, 278, 1992. (b.) S.L. Howard, R.C. Sausa, R.J. Locke, and A.W. Miziolek, Triple quadrupole mass spectrometry as applied to flame diagnostics: study of the $C_2H_4/N_2O/Ar$ flame, *Journal of the American Society of Mass Spectrometry* 4, 152, 1993. (c.) J.S. Bernstein, A. Fein, J.B. Choi, T.A. Cool, R.C. Sausa, S.L. Howard, R.J. Locke, and A.W. Miziolek, "Laser-based flame species profile measurements: a comparison with flame model predictions", *Combustion and Flame* 92, 85, 1993.

Appendix A: A list of publications/presentations is given. A copy of the journal publication, item (1), is attached to the hard copy version of this final report. If you have obtained this final report via a WORD file, look for files containing the journal publication in a subdirectory to the directory containing the final report file. The paper is contained in 7 WORD document files which are to be opened, printed, and assembled in the following order: ch3oh-acs5, appendix A, appendix B, appendix C, appendix D, Table-asc2, and Figs-asc2. Color printing is nice for the figures, if available, but not absolutely necessary.

Journal publication, peer reviewed:

(1) Wen-chium Ing, Chad Y. Sheng, and Joseph Bozzelli, "Detailed, Pressure Dependant Reaction Model for Methane/Methanol Mixtures Under Pyrolytic and Oxidative Conditions and Comparison with Experiment", Fuel Processing Technology, in press.

Conference/symposium presentations:

(2) C. Sheng and J.W. Bozzelli, "Thermochemistry, Reaction Paths and Kinetic Parameters in Hydrocarbon Pyrolysis and Oxidation," Symposium on Applications of Computational Chemistry in Petroleum Chemicals, ACS Meeting, Orlando, FL, April 2002.

(3) C. Sheng and J.W. Bozzelli, "Thermochemical Parameters, Enthalpies, Entropies and Heat Capacities of Hydrocarbons and Oxygenated Hydrocarbons Reactions Important in Chain Branching," 2002 International IUPAC Chemical conference on Thermodynamics, Rostock, Germany, July 22 – 26, 2002.

(4) W.R. Anderson, R.C. Sausa, and J.W. Bozzelli, "Novel Laser Ionization and Modeling Techniques for the Determination of Soot Nucleation Mechanisms," U.S. Army Industrial Ecology Information Exchange Meeting, Lake Harmony (Split Rock), PA, June 25-27, 2002.